

1 **Emerging Airborne Contaminants in India: Platinum Group Elements**
2 **from Catalytic Converters in Motor Vehicles**

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ABSTRACT

Platinum Group Element (PGE) pollution on the Indian subcontinent is a growing concern because vehicle sales in India have rapidly increased over the last decade, and it is well known that automobile catalytic converters are one of the major source of anthropogenic PGE in the environment. Despite the rapid growth of the Indian automobile industry, the sources and magnitude of PGE contamination in Indian airborne particles are unknown. In this study we report PGE and mercury (Hg) concentrations, as well as osmium isotope ratios ($^{187}\text{Os}/^{188}\text{Os}$) of airborne particles (PM_{10}) collected in Kanpur, a large industrial city in India. We estimate that $61\pm 22\%$, $32\pm 24\%$, and $7\pm 3\%$ of the total Os fraction are derived from eroding upper continental crust, catalytic converters fitted in the exhaust system of motor vehicles, and fossil fuel combustion, respectively. Only one sample had a ten times higher ($\sim 76\%$) than average contribution from fossil fuel. Unlike Os, Pt is predominantly ($84\pm 10\%$) derived from anthropogenic sources. Platinum Group Element and Hg concentrations are not well correlated. However, the highest concentration of particulate Hg corresponds to the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios (4.6). Our results further indicated that PGE/Ir ratios could be successfully used to quantify the relative proportions of natural and anthropogenic PGE sources in aerosol samples. Since PGE and Hg data on Indian environmental samples are scarce, this study provides an interpretive framework that calls for additional assessments of PGE and Hg concentrations in environmental samples from India.

1. INTRODUCTION

Human activities have significantly altered the biogeochemical cycles of Platinum Group Elements (PGE) (Sen and Peucker-Ehrenbrink, 2012). Mining, fossil fuel and biomass burning, construction, and human contributions to net primary productivity are moving 2 megagrams (1 Mg = 10^3 Kg) of Os, 5 Mg of Ir, 20 Mg of Ru, 40 Mg of Rh, and 187 Mg of Pt every year between different surficial geochemical reservoirs. Such large anthropogenic displacements of PGE are many orders of magnitude larger than mass transfer through natural processes such as riverine transport, primary production, wind erosion, volcanic eruption, sea-salt spray, and cosmic dust fluxes (Sen and Peucker-Ehrenbrink, 2012). As a result, the natural biogeochemical PGE cycles are disturbed. PGE derived from anthropogenic sources have been detected in snow, rainwater, soil, aerosols, vegetation and are no longer restricted to urban and rural locations (Barbante et al., 2001, Gómez et al., 2001, Gómez et al., 2002, Kanitsar et al., 2003, Whiteley et al., 2003, Morcelli et al., 2005, Rauch et al., 2005, Rauch et al., 2006, Hooda et al., 2007, Moldovan et al., 2007, Chen et al., 2009, Soyol-Erdene et al., 2011, Sen et al., 2013, Almécija et al., 2015). Anthropogenic PGE are found in some of the most pristine and isolated landmasses such as Antarctica (Soyol-Erdene et al., 2011). PGE are partially bioavailable in the environment (Schäfer et al., 1998, Wiseman and Zereini, 2009). For example, up to 30% of Pt emitted from catalytic converters is bioavailable in rats (Ek et al., 2004). Since PGE are bioavailable and studies have linked elevated concentrations of PGE in fine atmospheric particulate matter (PM_{2.5}) to increased morbidity and mortality rates, increasing PGE contamination is an emerging global concern (Wiseman and Zereini, 2009).

PGE in the environment can be derived from natural and anthropogenic sources (McCandless and Ruiz, 1991, Esser and Turekian, 1993, Palacios et al., 2000, Moldovan et al., 2002, Poirier and Gariépy, 2005, Rauch et al., 2009, Jackson et al., 2010, Baïoumy et al., 2011, Funari et al., 2016). The dominant source of anthropogenic PGE in the environment is thought to be catalytic converters in automobiles (Palacios et al., 2000, Moldovan et al., 2002). Catalytic converters are emission control devices that are installed in the exhaust system of vehicles and are used to reduce emissions of NO_x, CO, as well as partially burned and unburned hydrocarbons. The catalytic surfaces in these devices are primarily composed of Pt, Pd and Rh, whereas Os is present as a contaminant in trace amounts (Rauch et al., 2009, Poirier and Gariépy, 2005). During vehicle operation, PGE particles are thermally mobilized and mechanically abraded from the device and released into the environment. A substantial body of published information already exists on the sources and magnitudes of PGE pollution in North and South American countries (Rauch et al., 2005, Bocca et al., 2006, Rauch et al., 2006, Sen et al., 2013), China (Pan et al., 2009), and

European countries (Moldovan et al., 2006, Zereini et al., 2012). With the exception of very recently published study (Diong et al., 2016) that reports elevated Pt, Pd and Rh concentrations in PM_{2.5} and PM₁₀ samples from downtown Kolkata, studies on the sources and magnitude of PGE pollution in airborne particulate matter are still missing in India, despite the fact that PGE pollution is a growing concern there (Sen, 2013). Some anthropogenic processes that release PGE (fossil fuel combustion, mining and biomass burning) also emit mercury (Hg) at a global annual rate of 38±2.4 Gg (1 Gg = 10⁶ Kg), (Sen and Peucker-Ehrenbrink, 2012) yet limited information exists on concentrations and sources of Hg in airborne particulate matter in India. The sources of Os in the environment can be traced by using the Os isotope (¹⁸⁷Os/¹⁸⁸Os) composition, because potential natural and anthropogenic end-members have distinct ¹⁸⁷Os/¹⁸⁸Os ratios. For example, most anthropogenic sources such as catalytic converters and industrial waste have ¹⁸⁷Os/¹⁸⁸Os values ranging between 0.1-0.2 (Poirier and Gariepy, 2005), whereas eroding continental crust has an average ¹⁸⁷Os/¹⁸⁸Os value of ~1.2 (Peucker-Ehrenbrink and Jahn, 2001). Here, we report on PGE, Hg, and ¹⁸⁷Os/¹⁸⁸Os systematics of airborne particulate matter collected in Kanpur, a large industrial city in northern India. The main objective of the study is to understand the magnitude and source(s) of PGE contamination, as well as concentrations of Hg in airborne particulate matter in an area that is likely significantly contaminated. Our secondary aim is to investigate relationships between PGE and Hg, as anthropogenic Hg and PGE emissions share some (e.g. fossil fuel combustion), but not all (catalytic converters) emission sources. Hg concentrations might therefore be useful to refine PGE source apportionment. This study also provides a baseline and framework for future, more comprehensive studies of PGE contamination in India.

2. MATERIALS AND METHODS

2.1 Sample Collection:

Eleven aerosols were collected between March 1-21, 2013, using a high volume (1000 L/min) Envirotech PM₁₀ sampler (model number: APM 460 DXNL) on the campus of the Indian Institute of Technology Kanpur (IIT-K, latitude: 26°30'47.69" N; longitude: 80°13'56.39" E). The aerosol sampler was placed on the roof of a 15 m tall building. The sampler was used for ~9 hours each day between 9:00 AM to 6:00 PM (Indian Standard Time) and approximately 530 m³ of air per sample was pumped through each 20 cm x 25 cm preconditioned (heated at 550°C for 12 hours) quartz fiber Whatman™ filter (Table 1). The sampling site is ~16 km northwest of Kanpur City, one of the largest industrialized centers in Uttar Pradesh, India. The site is located

~5 Km North of a coal fired thermal power plant (Panki Thermal Power Plant) and a kilometer west of National Highway (NH-91). The types of vehicles using NH-91 include light and heavy trucks, buses, tractors, passenger cars and jeeps, motorcycles, and three-wheelers (Vikram auto rickshaw). It is estimated that on average every hour approximately 800 vehicles are passing in both directions on NH-91 in front of IIT Kanpur campus (Shukla et al., 2012).

In order to understand the source regions of the air parcel pumped through the filter, air mass trajectories were computed 12 hours back in time at 6 hour intervals from 12:00 UTC at an elevation of 500 m, 1000 m, and 1500 m above ground level during the sampling period using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model of the U.S. National Oceanic and Atmospheric Administration (Draxler and Rolph, 2003). The archived data file GDAS1 was used for computations. The aerosol-laden quartz fiber filters were dried at 50°C and then powdered using a ceramic shatter box that was preconditioned with quartz fiber material at Woods Hole Oceanographic Institution, and were analyzed for PGE, Hg and ¹⁸⁷Os/¹⁸⁸Os isotopes. Note that direct gravimetric analyses of PM₁₀ particles were not done and PM₁₀ concentration data are therefore unavailable. A different aliquot of the sample powder was also analyzed for Pb isotope ratios and trace metal compositions to understand the sources of atmospheric lead in Kanpur. The results of these analyses are reported in Sen et al. (2016).

2.2 Sample Preparation:

PGE were pre-concentrated from ~1.5-2 g of powdered filter paper (total weight of aerosol laden filter powder ~3.5 g) using the NiS fire assay technique (Ravizza and Pyle, 1997). Samples were only processed once, as the method consumed the entire sample split available for PGE analyses. PGE concentrations were determined by isotope dilution. Briefly, the sample powder was mixed with a solution enriched in the following isotopes: ¹⁹⁰Os, ¹⁰⁵Pd, ¹⁹¹Ir, and ¹⁹⁸Pt. This mixture was then fused with 5 g of nickel-sulfur-borax powder in a ceramic crucible at 1050°C for two hours. Nickel and sulfur formed an immiscible NiS melt, which extracted the PGE from the melt and cooled at the end of the experiment to form a solid NiS bead. The yields for the NiS bead were between 55%-75%. The NiS bead was isolated from the ceramic crucible, and thereafter dissolved in boiling ~6.2N HCl. Following the dissolution of the NiS bead, the ~6.2 N HCl solution was cooled and passed through a 0.45 µm cellulose filter paper to capture the insoluble PGE-rich particles. The 0.45 µm cellulose filter paper that contained the PGE-rich particles was stored in acid cleaned Teflon beakers. Additional details of the NiS fire assay technique can be found in Ravizza and Pyle (1997). On the day of analysis, 1 mL of concentrated HNO₃ was added to the filter paper, and the clean beaker was placed on a hotplate at ~130°C for

60 minutes. Afterwards, the sample solution was chilled and diluted ~5-fold with 18.2 MΩ cm water from a Millipore water purification system.

2.3 ¹⁸⁷Os/¹⁸⁸Os and PGE Analyses:

The ¹⁸⁷Os/¹⁸⁸Os isotope and PGE analyses were carried out in the Woods Hole Oceanographic Institution Inductively-Coupled Plasma Mass Spectrometry Facility (WHOI-ICPMS Facility). For Os analysis, volatile OsO₄ dissolved in the sample vial was extracted by bubbling Ar gas through the sample solution, also known as sparging technique (Hassler et al., 2000). The sparged OsO₄ was analyzed with a multicollector inductively coupled plasma mass spectrometer (MC-ICPMS, ThermoScientific NEPTUNE). The ¹⁸⁷Os/¹⁸⁸Os and Os concentrations were determined with the established data acquisition and reduction techniques in the WHOI-ICPMS Facility (Sen and Peucker-Ehrenbrink, 2014). Leoben (Austria) Os standard (LOsSt) was repeatedly analyzed during sample analysis to assess the quality of data. Repeat analyses of 5 pg Os (LOsSt) yielded an average ¹⁸⁷Os/¹⁸⁸Os of 0.1115±0.0009 (95% confidence interval, n=5), which is slightly more radiogenic than previously reported values for LOsSt (0.1067±0.0019) (Sen and Peucker-Ehrenbrink, 2014). Given the large dynamic range of Os isotope values determined in this study, the slight discrepancy between our very low level analyses and previously determined values does not affect the interpretation of our data.

Iridium and Pt abundances were measured using a single-collector magnetic sector ICPMS (ThermoScientific Element2). Since Pd concentrations calculated based on the mass/charge ratios of 105/106 and 105/108 are not in agreement, likely due to interferences from ZrO, ZnAr and/or Cd, we do not report Pd concentrations. Mass/charge ratio of 191/193 was used to calculate Ir concentration, whereas Pt concentration was calculated based on the mass/charge ratios of 198/194 and 198/195. During the analysis, ²⁰⁰Hg was monitored to correct ¹⁹⁸Hg interferences on the 198/195 mass charge ratios. Since the natural ¹⁹⁸Hg/²⁰⁰Hg atom ratio is 0.43 and ²⁰⁰Hg count rates are ~2000 counts per second (cps) a correction of less than 430 cps should appear at the mass/charge 198. Based on typical count rates on ¹⁹⁸Pt, Hg interferences are small, likely about one percent. The Pt concentration calculated from both ratios agree within 7% and we are reporting the slightly lower Pt concentration obtained from mass/charge ratio 198/195. The total procedural blanks from the filter papers and nickel-sulfur-borax powder were 15 ± 9 pg/g for Pt, 0.4 (+0.7, -0.4) pg/g for Ir, and 0.49 ± 0.05 pg/g for Os (n=3, 2 S.D.). The ¹⁸⁷Os/¹⁸⁸Os composition of the blank was 0.78 ± 0.05 (n=3, 2 S.D.). The analytical methods for measuring PGE concentrations using a single-collector magnetic sector ICPMS (ThermoScientific Element2) have been carefully evaluated with in-house standards in 5% HNO₃ and reference

materials (see Peucker-Ehrenbrink et al., 2003 and Rauch et al., 2005). For example, the same analytical method, filter papers and mixture of nickel-sulfur-borax powder was used to determine the PGE concentrations in tunnel dust reference material BCR-723 and the results (Pt = 97 ng/g, certified value: 81.3±3.3) were in good agreement with the certified values (Rauch et al., 2005). A detailed assessment of PGE uncertainties in samples with low PGE concentrations is provided in Peucker-Ehrenbrink et al., (2003). Here we report the blank-corrected concentration data that were converted to mass/m³ of each element by dividing the blank-corrected concentrations by the total volume of air that was pumped through the filter paper.

2.4 Hg Analysis and Data Quality

Particulate Hg collected on filters was analyzed in University of South Carolina with a portable Hg vapor analyzer (Lumex, Model RA-915+/PYRO-915+, St. Petersburg, Russia) using thermal decomposition, amalgamation and atomic absorption spectrophotometry (AAS) without the need for pre-digestion steps (USEPA, 2007). Standards analyzed included IAEA-086 (human hair) and NIST Standard Reference Material 1515 (apple leaves), and recovery averaged 87.9%±4.1% (1 S.D.) and 85.9%±3.6% (1 S.D), respectively. Filters were analyzed in duplicate; the relative percent difference averaged 2.0±1.1%. The filter blank concentration was 0.25 ± 0.15 ng/g, which represented 0.56±0.19% of the total Hg concentration of the analyzed filters, and therefore insignificant.

3. Results

¹⁸⁷Os/¹⁸⁸Os isotope ratios, PGE and Hg concentrations of PM₁₀ aerosols from Kanpur are reported in Table 1. The Os, Ir, Pt, and Hg concentrations vary in the range 0.009-0.051 pg/m³, 0.009-0.058 pg/m³, 2.5-11.9 pg/m³, and 0.19-0.45 ng/m³, respectively, with one sample (19-Mar-13) having an order of magnitude higher concentrations of Ir and Pt (but not Os) than the other samples. The PGE concentrations in Kanpur are similar to those reported for other urban centers, and almost an order of magnitude higher than rural areas (Figure 1). The aerosols are enriched in Pt relative to Os and Ir, and show strongly fractionated PGE abundance patterns. For example, the Pt/Os ratios vary between 68-5659 (Table 1), and the PGE ratios are qualitatively similar to the patterns observed in other urban aerosols (Rauch et al., 2006, Qi et al., 2011, Sen et al., 2013). Concentrations of individual PGE do not correlate with each other. Particulate Hg concentrations are similar to the reported values for industrial cities in China (0.34-5.8 ng/m³) and Europe (0.05-3.14 ng/m³) (Vassilakos et al., 2007, Araujo et al., 2011).

The $^{187}\text{Os}/^{188}\text{Os}$ ratios vary from 0.39 to more radiogenic values of 0.94, and one sample has an extremely radiogenic value of 4.6 (Figure 2). Such large variations in the $^{187}\text{Os}/^{188}\text{Os}$ composition have been reported previously. For example in Boston, USA, $^{187}\text{Os}/^{188}\text{Os}$ varies between 0.30 and 2.83 (Rauch et al., 2005). The $^{187}\text{Os}/^{188}\text{Os}$ values positively correlate with reciprocal ^{188}Os concentrations, a correlation indicative of two-component mixing. A single sample (21-Mar-13) with extremely radiogenic $^{187}\text{Os}/^{188}\text{Os}$ does not fall on the correlation that is defined by the rest of the samples, indicating contributions from at least three distinct sources. Air-mass back trajectory computations using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model of the U.S. National Oceanic and Atmospheric Administration (Draxler and Rolph, 2003) reveal that the air masses are coming from the northwestern part of India, except for sample numbers 13-Mar-13 and 14-Mar-13 that represent air from the South-Southeast, and for sample number 21-Mar-13 that has a trajectory from the Northeast (Figure S1, supporting information). It is worth mentioning in this context that the air mass trajectories of the very radiogenic sample with high Hg concentrations come from a northeastern direction, whereas for all other samples the air masses are coming either from the northwest, south or southeast of the sampling site (Figure S1, supporting information).

4. Discussion

We summarize the key observations of our geochemical study as (1) the aerosols show a large range in $^{187}\text{Os}/^{188}\text{Os}$ from unradiogenic (0.386) to radiogenic (4.6) values that positively correlate with reciprocal ^{188}Os concentrations, and (2) PGE concentrations in Kanpur are almost an order of magnitude higher when compared to rural areas and have Pt/Os that are very high (68-5659) when compared to eroding continental crust. These observations imply that PGE are derived from multiple, including anthropogenic, source(s).

4.1 Natural vs. Anthropogenic PGE Signature:

PGE concentration ratios can be used to differentiate between natural and anthropogenic signatures (Zereini et al., 2004, Rauch et al., 2005, Pan et al., 2009, Sen et al., 2013). For example, average Pt/Os ratios of eroding continental crust and uncontaminated soil vary between 6-43 (Schmidt et al., 1997, Qi et al., 2011, Peucker-Ehrenbrink and Jahn, 2001), whereas the aerosols collected in Kanpur have much higher Pt/Os ratios (68-467, with one sample ~5659). This implies that PGE are not primarily derived from natural source(s). Eroding continental crust, which can be used as a proxy for natural aeolian dust, has a $^{187}\text{Os}/^{188}\text{Os} \sim 1.2$ (Peucker-Ehrenbrink

and Jahn, 2001). The $^{187}\text{Os}/^{188}\text{Os}$ values of aerosols collected in Kanpur vary between 0.39 and 4.6, indicative of contributions from unradiogenic as well as very radiogenic anthropogenic sources. Therefore, both the PGE systematics and $^{187}\text{Os}/^{188}\text{Os}$ values indicate that the PGE are derived – in part - from anthropogenic sources.

4.2 Anthropogenic Sources of PGE

Airborne PGE chemistry can be best explained by mixed contributions from natural and anthropogenic sources. The natural sources include aeolian dust (Peucker-Ehrenbrink and Jahn, 2001), volcanic eruption (Zoller et al., 1983, Yudovskaya et al., 2008), and cosmic dust (Peucker-Ehrenbrink and Ravizza, 2000, Gabrielli et al., 2006), while the major anthropogenic sources include automobile catalytic converters (Poirier and Gariepy, 2005), industrial and hospital waste (Peucker-Ehrenbrink and Ravizza, 2000, Williams and Turekian, 2002, Funari et al., 2016), smelting of PGE and chromite ores (McCandless and Ruiz, 1991, Walker et al., 1994), smelting of base metal sulfide ores (e.g., Cu, Ni, Zn and Pb) (Walker et al., 1994, Morgan et al., 2002), and fossil fuel burning (Selby et al., 2007, Baioumy et al., 2011). Combining $^{187}\text{Os}/^{188}\text{Os}$ values and PGE concentration ratios is a particularly powerful means of identifying PGE sources (e.g. Rauch et al., 2006, Sen et al., 2013). The $^{187}\text{Os}/^{188}\text{Os}$ values of loess and other poorly weathered sedimentary deposits at the Earth's surface serve as a proxy for natural eolian dust composition (Peucker-Ehrenbrink and Jahn, 2001). $^{187}\text{Os}/^{188}\text{Os}$ values of most anthropogenic end-members are well defined. For example, catalytic converter-derived PGE and industrial waste are characterized by unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ (0.1-0.2) (Poirier and Gariepy, 2005). Unradiogenic Os can also be released by medical facilities (Esser and Turekian, 1993) where it is used to stain and prepare tissues for transmission electron microscopy. In contrast, ore deposits can have unradiogenic to radiogenic $^{187}\text{Os}/^{188}\text{Os}$. Chromite ores and PGE ores that are predominantly derived from deposits in mafic-ultramafic mantle-derived rocks are characterized by unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ (0.1-0.2) (McCandless and Ruiz, 1991, Walker et al., 1994). In contrast, $^{187}\text{Os}/^{188}\text{Os}$ values of base metal sulfide ores range from extremely unradiogenic (~ 0.1) to radiogenic values (>1) (Walker et al., 1994, Morgan et al., 2002). Coal (Baioumy et al., 2011) and crude oil (Morgan et al., 2002, Selby et al., 2007) are generally characterized by radiogenic $^{187}\text{Os}/^{188}\text{Os}$ (>1.2) because of their high Re/Os ratios. As the $^{187}\text{Os}/^{188}\text{Os}$ compositions of potential end-members overlap, additional proxies need to be used for reliable PGE source apportionment.

In figure 2 we show that the combination of Pt/Os and $^{187}\text{Os}/^{188}\text{Os}$ can be used to trace PGE sources. Since catalytic converters are mainly composed of Pt, Pd and Rh, with Os present only as an impurity, particles emitted from catalytic converters during vehicle operation should

have very high Pt/Os ratios. Eroding continental crust, in contrast, has a Pt/Os value of ~6.5, whereas Pt/Os ratios of uncontaminated soils vary between 6 and 43. Figure 2 shows that the Pt/Os and $^{187}\text{Os}/^{188}\text{Os}$ of roadside soils overlap with Kanpur aerosols, which indicates a catalytic converter source, because materials abraded from catalytic converters during vehicle operation are concentrated in the roadside environment. Ir/Os and Pt/Os systematics (figure 3) support this inference.

4.3 Hg in Airborne Particulate Matter

Over half of the global Hg emission comes from Asian countries, including India (Li et al., 2009), yet limited information exists on the Hg concentrations of airborne particulate matter from India. In India, the total Hg concentration in air (including particulate-bound, elemental and reactive Hg) can be as high as 41.5 ng/m³ (Krishna Murti, 1987), which is 24 times higher than the global background average for total Hg (1.5-1.7 ng/m³, Lindberg et al., 2007). Studies from India investigating Hg contamination in water, sediment, and fish samples (e.g., Li et al., 2009, Krishna Murti, 1987) suggest anthropogenic contamination (Li et al., 2009). Although limited in number, the Kanpur aerosols have elevated concentration of Hg (0.19-0.45 ng/m³) compared to Hg concentrations in airborne particles in remote and pristine environments (e.g., 0.04 ng/m³, Krishna Murti, 1987, Arimoto et al., 2004). With one exception, Hg concentrations do not correlate with PGE concentrations, suggesting Hg is derived from different sources, or is carried on different particles. Gaseous forms of Hg, such as elemental Hg, which is more than 95% of total Hg (Lindberg et al., 2007), may not be captured on the quartz-fiber matrix (Lu and Schroeder, 1999; Arimoto et al., 2004). It is worth mentioning that the highest concentrations of particulate Hg and Os correspond to the sample with the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio. This suggests a common source for Hg and Os isotopes, possibly coal combustion (Morgan et al., 2002, Baioumy et al., 2011), which is the major source of anthropogenic Hg emissions (Sen and Peucker-Ehrenbrink, 2012) and since the sampling site is ~5 Km North of a coal fired thermal power plant.

4.4 Assessment of Anthropogenic Sources of PGE

$^{187}\text{Os}/^{188}\text{Os}$ values can be used to quantify the fraction of anthropogenic Os in the total Os elemental budget (Rauch et al., 2005). However, $^{187}\text{Os}/^{188}\text{Os}$ of anthropogenic end-members can range from unradiogenic (~0.1) (Poirier and Gariépy, 2005) to radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values (>1) (Selby et al., 2007, Baioumy et al., 2011), encompassing the natural end-member composition ($^{187}\text{Os}/^{188}\text{Os} \sim 1.2$) (Peucker-Ehrenbrink and Jahn, 2001) as discussed in section 4.2. In order to

understand the relative Os contributions from multiple anthropogenic sources to the total Os budget, we either have to compute 3-component isotope mixing relationships (radiogenic anthropogenic source, unradiogenic anthropogenic source, and natural source; e.g. Rauch et al., 2009) or first quantify the anthropogenic and natural proportions, followed by a 2-component mixing model that distinguishes between radiogenic and unradiogenic anthropogenic sources. This study follows the second approach and uses PGE/Ir ratios to first calculate the relative anthropogenic and the natural PGE contributions in all samples. Since hydrocarbons and catalytic converters are characterized by very low (pg/g) concentrations of Ir, and Ir is non-volatile in surficial environments, our assumption is that almost all Ir is of natural origin. The anthropogenic proportion of total Os and Pt were calculated using the following equations:

$$Os_{\text{Anthropogenic}} = Os_{\text{Sample}} - [Ir_{\text{Sample}} \times [Os_{\text{Eroding Continental Crust}}/Ir_{\text{Eroding Continental Crust}}]] \quad (1)$$

$$Pt_{\text{Anthropogenic}} = Pt_{\text{Sample}} - [Ir_{\text{Sample}} \times [Pt_{\text{Eroding Continental Crust}}/Ir_{\text{Eroding Continental Crust}}]] \quad (2)$$

We assume the Os/Ir and Pt/Ir ratios of the eroding continental crust as 0.5 and 17, respectively (Schmidt et al., 1997, Peucker-Ehrenbrink and Jahn, 2001). The calculation shows that $61 \pm 22\%$ ($n=8$, 1 S.D.) of the total Os and $84 \pm 10\%$ ($n=11$, 1 S.D.) of the total Pt in our samples are anthropogenic in origin. In order to further quantify the relative proportions of different anthropogenic sources, we first calculate the $^{187}\text{Os}/^{188}\text{Os}$ value of the anthropogenic fraction ($^{187}\text{Os}/^{188}\text{Os}_{\text{anthropogenic fraction}}$) by subtracting natural Os from bulk Os, assuming that the $^{187}\text{Os}/^{188}\text{Os}$ composition of eroding continental crust (~ 1.2) is representative of natural Os carried by aerosols. Thereafter, we use a 2-component mixing model with catalytic converters (unradiogenic $^{187}\text{Os}/^{188}\text{Os}$) and fossil fuel (radiogenic $^{187}\text{Os}/^{188}\text{Os}$) as end-members. We assume the $^{187}\text{Os}/^{188}\text{Os}$ composition of catalytic converter and fossil fuel end member as 0.2 (Poirier and Gariépy, 2005) and 5.5 (Morgan et al., 2002, Selby et al., 2007), respectively. The relative proportion of catalytic converter contribution to anthropogenic Os budget was calculated using the following equation:

$$P_{Os \text{ CC}} = [(^{187}\text{Os}/^{188}\text{Os})_{\text{FF}} - (^{187}\text{Os}/^{188}\text{Os})_{\text{Anthropogenic fraction}}] \div [(^{187}\text{Os}/^{188}\text{Os})_{\text{FF}} - (^{187}\text{Os}/^{188}\text{Os})_{\text{CC}}] \times 100 \quad (3)$$

where $P_{Os \text{ CC}}$ = Relative proportion of Os sourced from catalytic converters; CC=Catalytic Converter; FF=Fossil Fuel.

The calculation reveals that $32 \pm 24\%$ of the total Os is sourced from catalytic converters, and $7 \pm 3\%$ from fossil fuel source. The only exception is sample 21-Mar-13, which had a 76% contribution from a fossil fuel source, consistent with its high Hg concentration. The results of the source apportionment of Os and Pt are given in Table 1. The quantitative results are strongly dependent on the choice of end-member compositions. For example,

if we use the upper continental crust estimates of Chen et al. (2016) we would have found that most Os is of natural origin. This finding is caused by the less radiogenic nature of the upper crustal $^{187}\text{Os}/^{188}\text{Os}$ of 0.8 that Chen et al. (2016) reported by determining the $^{187}\text{Os}/^{188}\text{Os}$ composition for glacial diamictites. We argue that our value of 1.2, determined for eolian loess deposits in China, South America and Europe, is a more suitable proxy for modern aerosols than Phanerozoic glacial sediments.

5. Summary

This study demonstrates that the observed PGE signatures in Kanpur aerosols in part reflect anthropogenic inputs. We estimate that $84\pm 10\%$ ($n=11$, 1 S.D.) of the total Pt fraction is anthropogenic in origin, and $32\pm 24\%$ and $7\pm 3\%$ of the total Os budget is sourced from catalytic converters and fossil fuel sources, respectively. The only exception is sample 21-Mar-13, which is characterized by very radiogenic $^{187}\text{Os}/^{188}\text{Os}$ composition (4.60) and high particulate Hg concentration. 76% of the total Os in this particular sample is derived from fossil fuel combustion. This study further demonstrates that the relative contribution of each source can be quantified using PGE/Ir and $^{187}\text{Os}/^{188}\text{Os}$ values. This quantification technique is simpler than multi-component isotope mixing models that rely on knowing, or assuming, end-member concentrations and isotope compositions. We argue that this approach provides a more robust means of quantifying the relative contribution of natural and anthropogenic sources in aerosol samples.

Since overall motor vehicle sales in India have grown rapidly ($\sim 15\%$ /year) over the last few years, the magnitude of PGE contamination is expected to increase in India. Two- and three-wheelers (known as auto rickshaw in India) also contribute substantially to PGE pollution, since EURO 2 emission norms require the use of catalytic converters in these motor vehicles. Between 2005 and 2011, sales of two-wheelers have increased by 100%, and release of PGE during vehicle operation will likely continue to rise, creating growing concern in India (Sen et al., 2013). Unfortunately, PGE data for Indian soil, plants, water, sediments and airborne particles are scarce, which currently limits our ability to quantify the magnitude of environmental PGE contamination in India. Additional assessments of PGE concentrations and $^{187}\text{Os}/^{188}\text{Os}$ compositions of Indian environmental samples should therefore be undertaken.

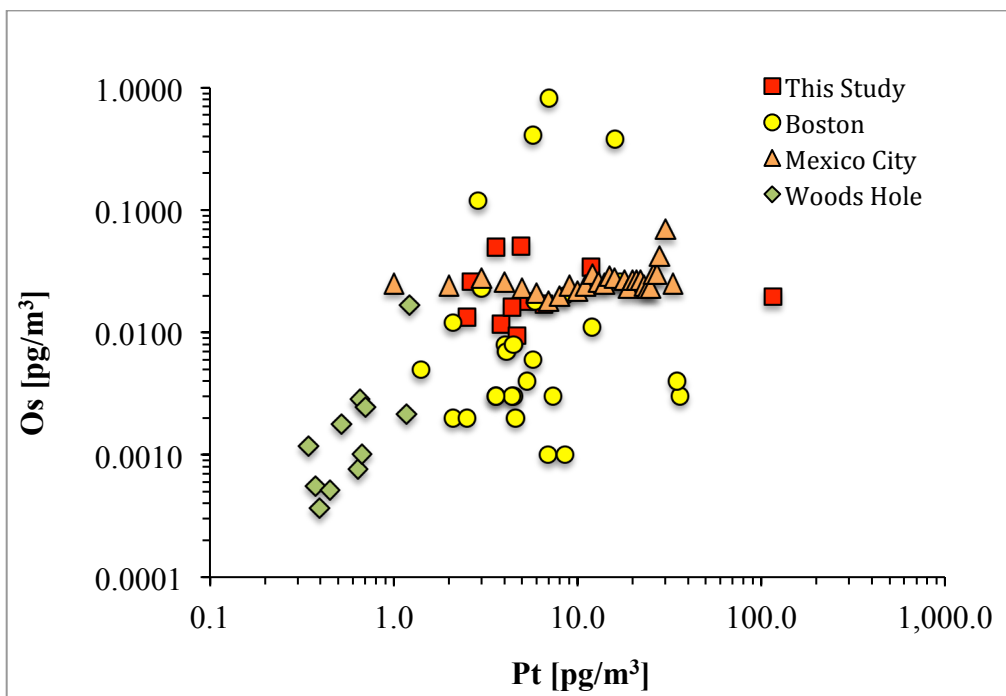
Supporting Information

359 Figure S1 shows the backward air mass trajectories of each sample computed using the HYSPLIT
360 trajectory model from the U.S. National Oceanic and Atmospheric Administration's (NOAA)
361 website.

362 **Acknowledgments**

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365 Facility.

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Figure 1: Plots of Os against Pt concentrations in airborne particles from Kanpur compared with urban airborne particulate matters from other areas. PGE concentrations in aerosols vary by several orders of magnitude. The data references are as follows: Boston (Rauch et al., 2005), Mexico City (Rauch et al., 2006), and Woods Hole (Sen et al., 2013).

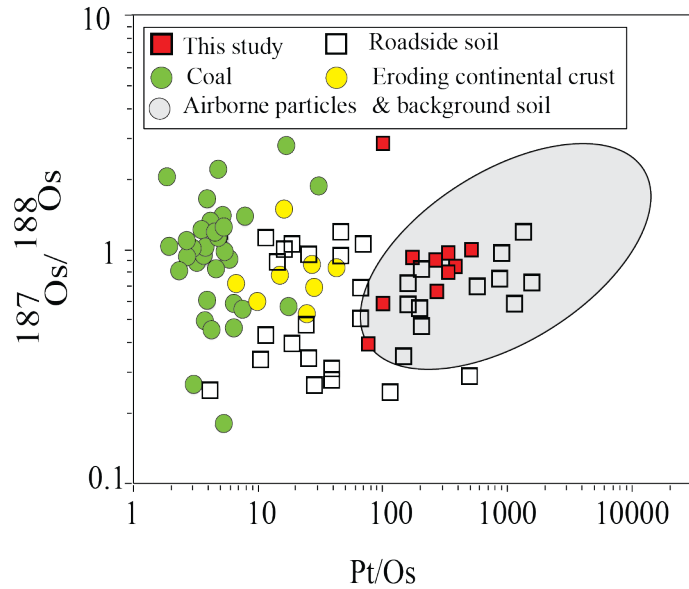


Figure 2: $^{187}\text{Os}/^{188}\text{Os}$ vs. Pt/Os of Kanpur aerosols [this study]. Kanpur aerosols overlap with roadside dust, and their signature does not match other plausible natural and anthropogenic sources. The data references are as follows: airborne particles (Rauch et al., 2005, Rauch et al 2006, Qi et al., 2011, Sen et al., 2013), eroding continental crust and background soil (Peucker-Ehrenbrink and Jahn, 2001, Qi et al., 2011, Chen et al., 2016), roadside dust represents the automobile catalyst-derived material; fossil fuels (Schafer et al., 1998, Qi et al., 2011), and coal (Baoumy et al., 2011).

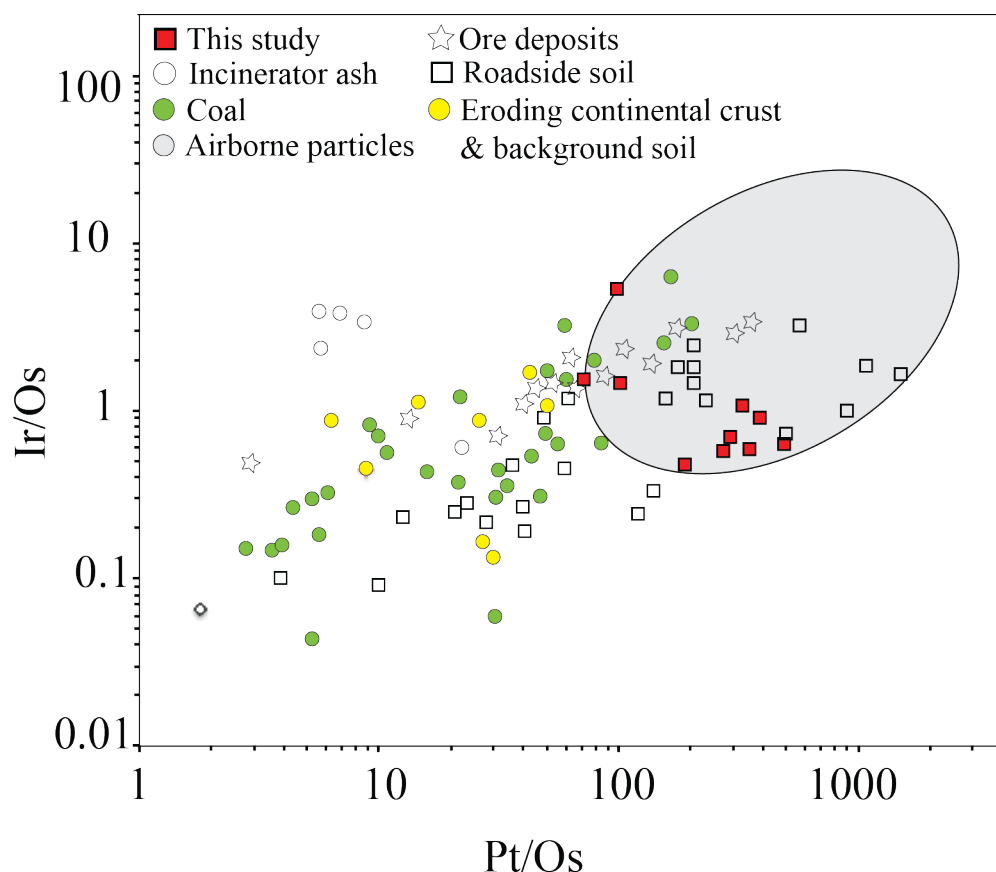


Figure 3: Pt/Os vs. Ir/Os for Kanpur aerosols (red squares, this study). The PGE concentrations ratios are compared to potential anthropogenic and natural sources. The potential anthropogenic end-members include catalyst-derived materials, coal, ore deposits, and incinerator ash. Average eroding continental crust and background levels in uncontaminated soils represent the natural end-member. The data references are as follows: eroding continental crust and background soil (Wedepohl, 1995, Schmidt et al., 1997, Qi et al., 2011, Peucker-Ehrenbrink and Jahn, 2001), coal (Qi and Gao, 2008, Baioumy et al., 2011), ore deposits (Naldrett, 2004, Qi and Gao, 2008), and automobile catalyst-derived material (Fritsche and Meisel, 2004, Qi et al., 2011). The grey field represents the range of PGE ratios in aerosols (Rauch et al., 2006, Qi et al., 2011, Sen et al., 2013).

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Table 1: Os isotope ratios and PGE, as well as Hg concentrations in PM₁₀ aerosols

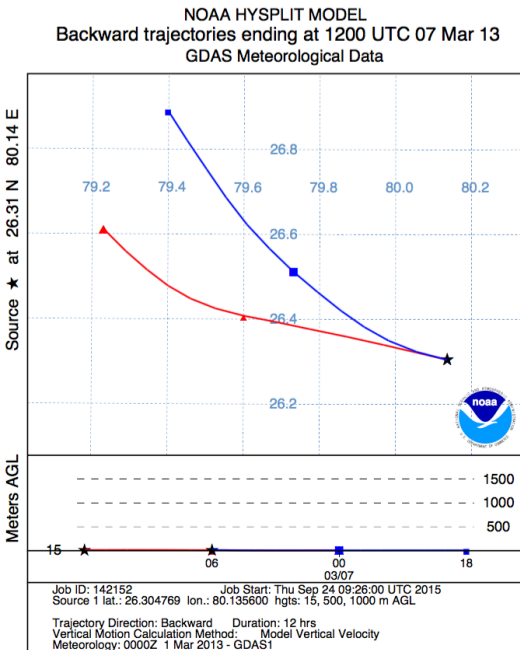
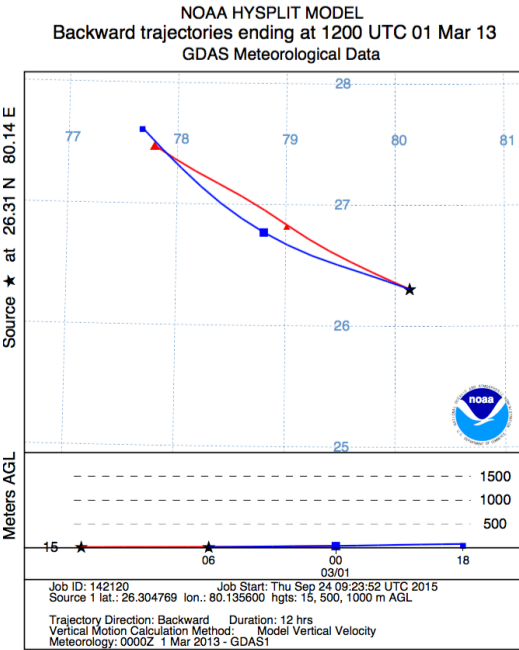
Sample No.	Vol. of air	¹⁸⁷ Os/ ¹⁸⁸ Os	±2σ	¹⁸⁸ Os	Os	Ir	Pt	Hg	Os/Ir	Os	Os	Os	Pt/Os	Pt
day-month-yr	sampled [m ³]		(abs.)	[pg m ⁻³]	[pg m ⁻³]	[pg m ⁻³]	[pg m ⁻³]	[ng m ⁻³]		Natural	Catalytic Converter	Fossil Fuel		Anthropogenic
1-Mar-13	528	0.90	0.018	0.0014	0.012	0.01	3.6	0.32	1.1	47%	45%	8%	306	92%
7-Mar-13	528	0.39	0.023	0.0064	0.050	0.03	3.4	0.20	1.5	33%	66%	1%	68	75%
8-Mar-13	528	0.89	0.013	0.0021	0.018	0.03	4.9	0.19	0.7	71%	22%	7%	274	86%
12-Mar-13	534	0.67	0.045	0.0020	0.016	0.03	4.2	0.19	0.6	86%	3%	11%	258	83%
13-Mar-13	528	0.89	0.015	0.0016	0.013	0.04	2.4	0.35	0.4	*	*	*	177	61%
14-Mar-13	545	0.85	0.015	0.0021	0.017	0.02	6.3	n.d.	0.9	56%	38%	6%	370	92%
15-Mar-13	545	0.84	0.012	0.0041	0.034	0.06	11.3	0.31	0.6	84%	11%	5%	331	87%
16-Mar-13	545	0.94	0.018	0.0011	0.009	0.01	4.4	0.33	0.6	78%	11%	11%	467	91%
18-Mar-13	545	0.59	0.013	0.0032	0.026	0.02	2.5	n.d.	1.5	34%	62%	4%	96	82%
19-Mar-13	534	0.72	0.010	0.0024	0.020	0.70	110.9	0.35	0.03	*	*	*	5659	84%
21-Mar-13	528	4.6	0.056	0.0042	0.051	0.01	4.7	0.45	5.3	9%	15%	76%	92	95%

n.d. Not determined; anthropogenic Os and Pt were calculated based on equation 1, 2 and 3

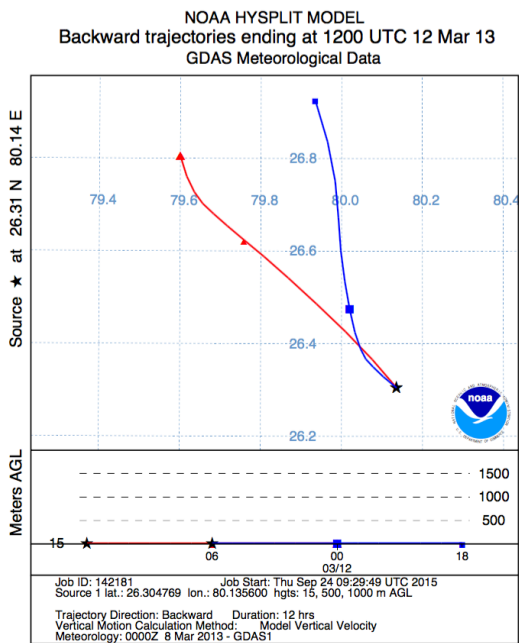
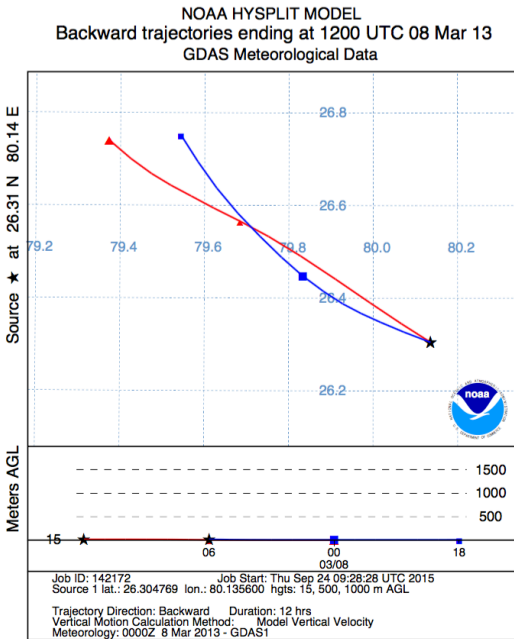
* the assumption that all Ir is natural may not be valid because of high Ir concentration

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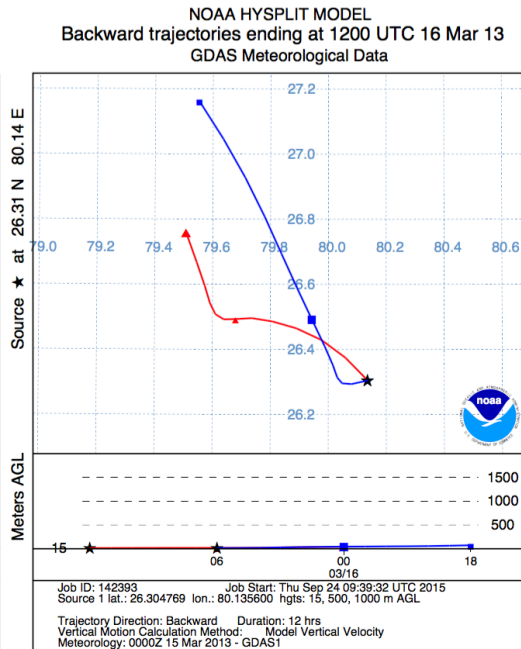
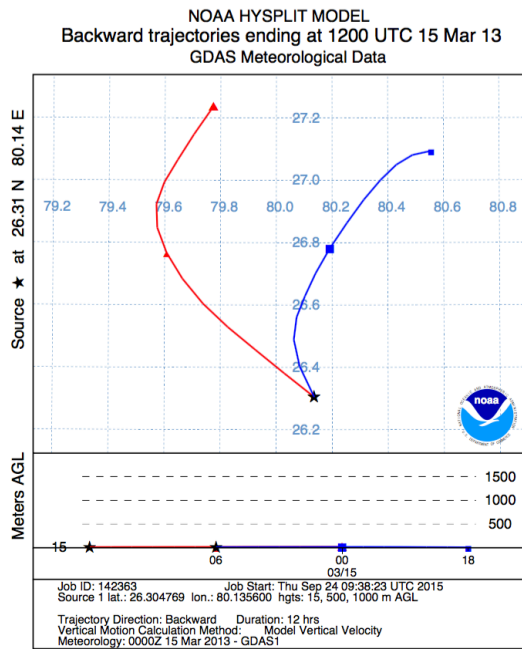
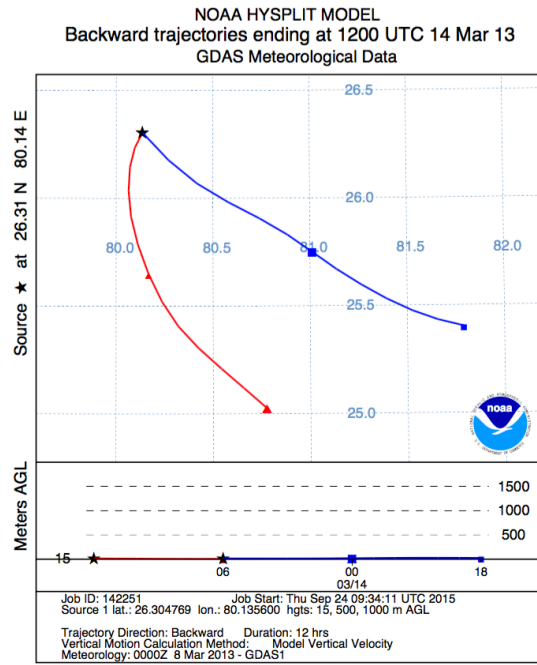
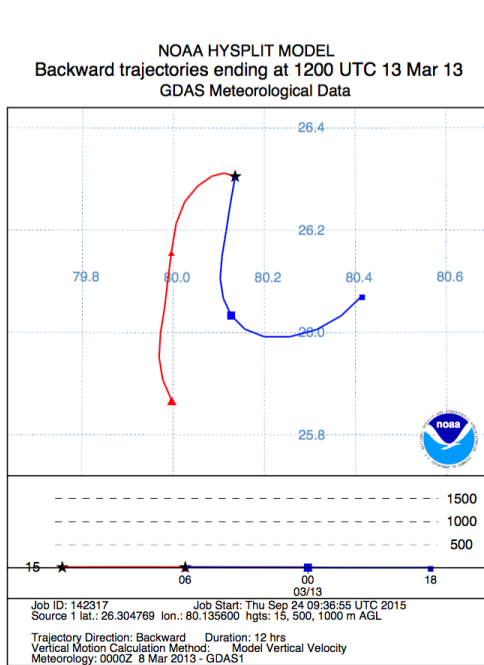
Supplementary Figure S1:



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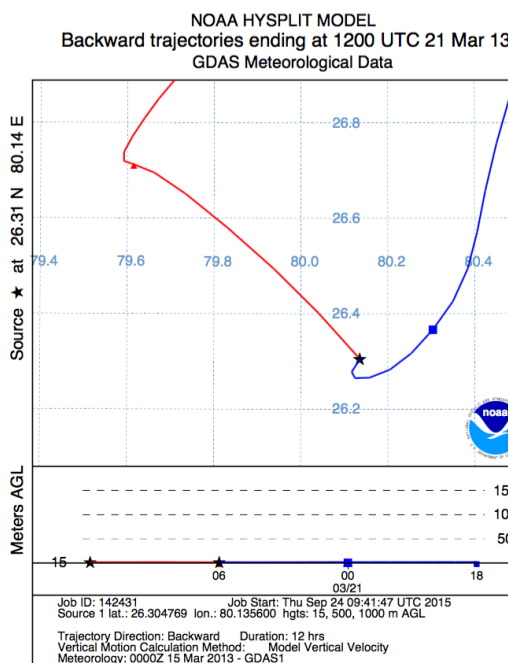
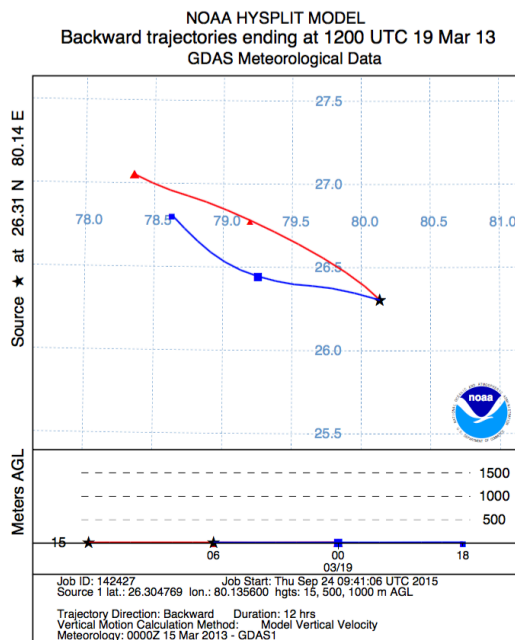
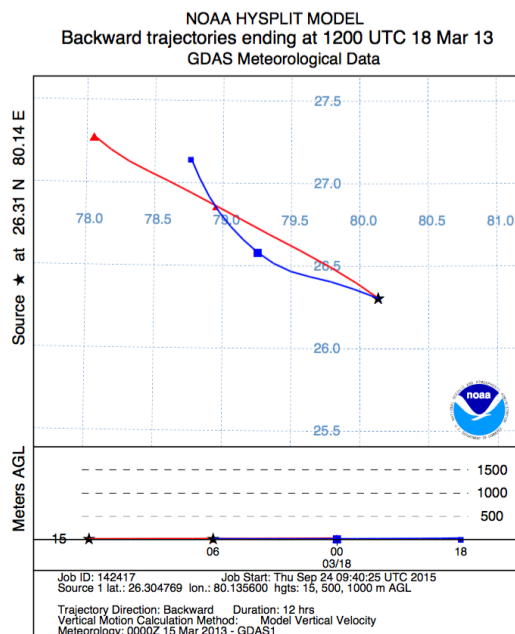


Figure S1: Air mass back trajectories for each sample. The trajectories were computed 12 hours back in time at an elevation of 500 m, 1000 m, and 1500 m above ground level during the sampling period using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) data from the U.S. National Oceanic and Atmospheric Administration's (NOAA) website. The archived data file GDAS1 was used. The figure shows that the air masses are mostly coming from northwestern side. Only for sample number 13-Mar-13 and 14-Mar-13 it is coming from south and southeast, and for 21-Mar-2013 one of the air mass trajectory is coming from northeastern.